Electronic Supplementary Material (ESI) for Nanoscale.

$FePO_4$ Supported Rh Subnano Clusters with Dual Active Sites for Efficient Hydrogenation of Quinoline under Mild Conditions

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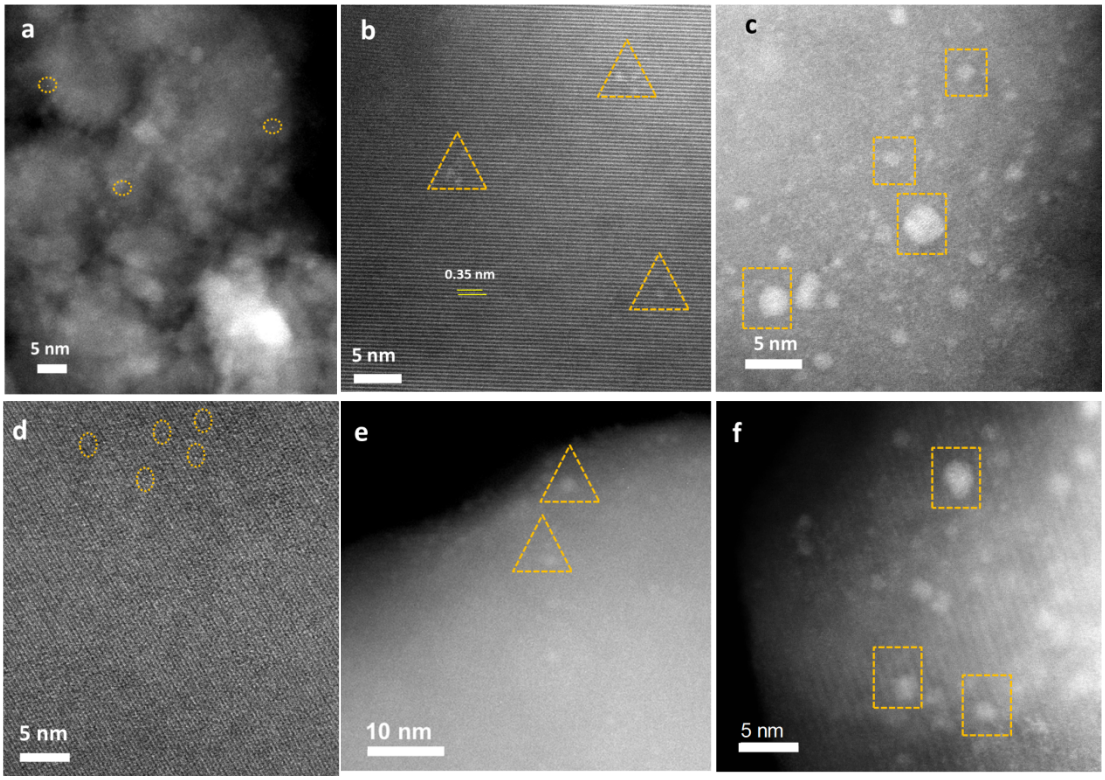

Fig. S1 AC-HAADF-STEM images of 0.08%Rh/$FePO_4$ (a,d), 0.8%Rh/$FePO_4$ (b,e) and 2.2%Rh/$FePO_4$ (c,f). The Rh single atoms, subnano clusters and nanoparticles are marked by circle, triangle and square, respectively. The lattice distance of 0.35 nm is assigned to the (102) facet of $FePO_4$ support.

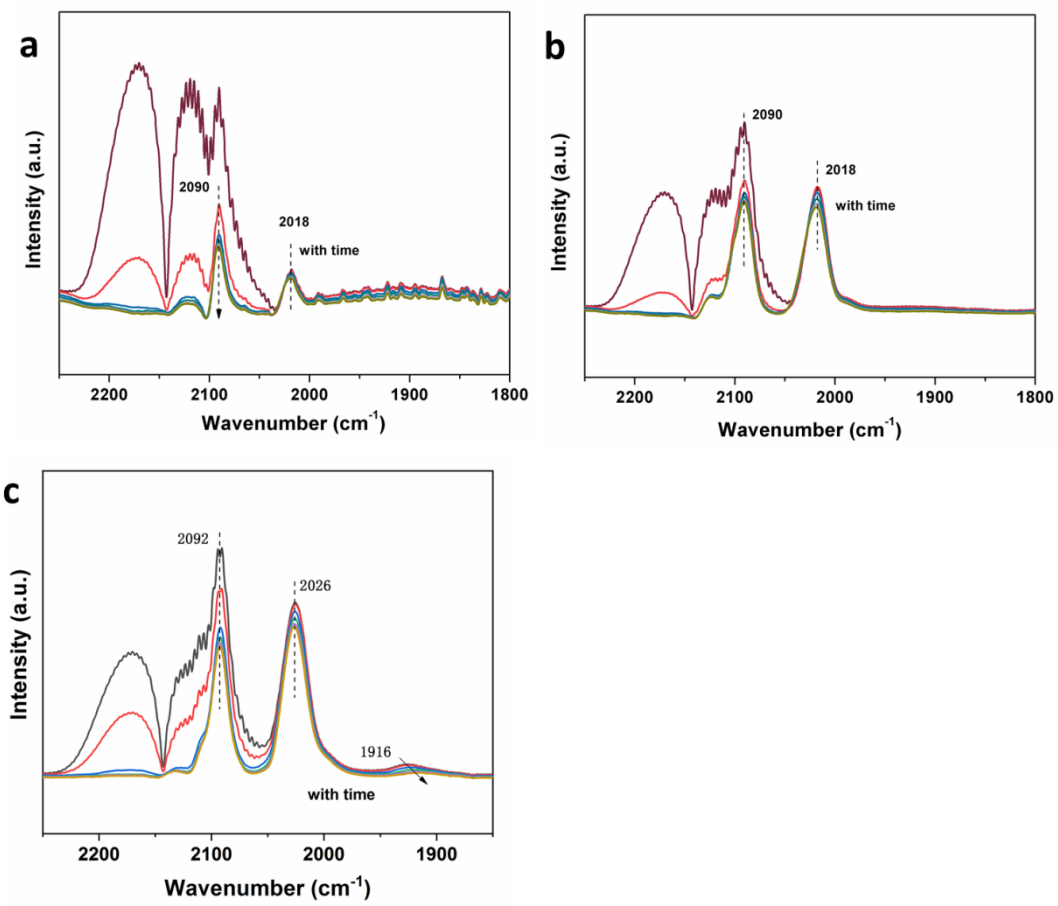

Fig. S2 The evolution of CO adsorption DRIFT spectra along with He purging over 0.08%Rh/$FePO_4$ (a), 0.8% Rh/$FePO_4$ (b) and 2.2% Rh/$FePO_4$ (c).

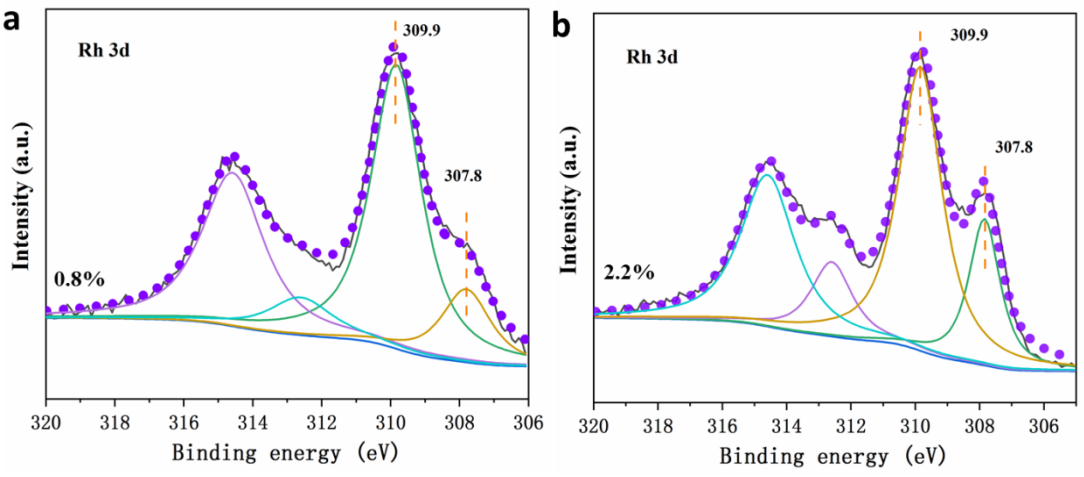

Fig. S3 XPS analysis of Rh 3d signal for 0.8%Rh/$FePO_4$ (a) and 2.2%Rh/$FePO_4$ (b).

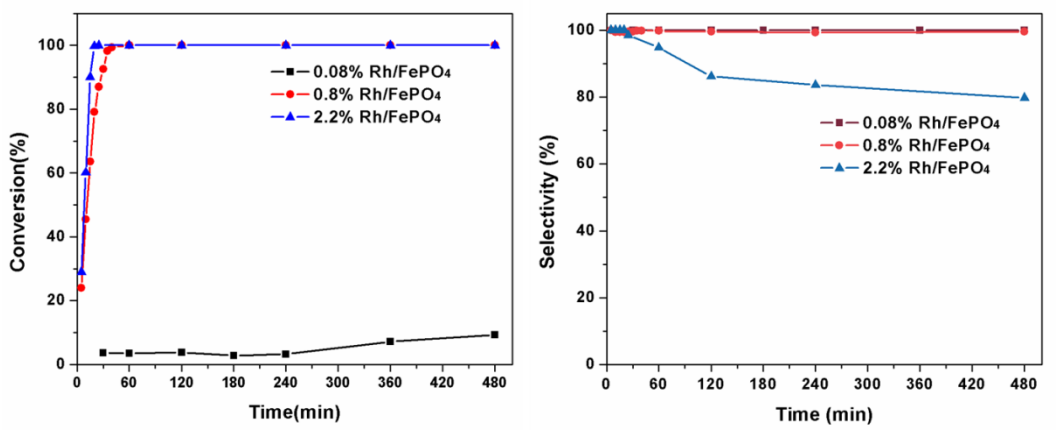

Fig. S4 Kinetic experiments of different Rh loading catalysts for the hydrogenation of quinoline. Reaction condition: 0.05 g 2.2%Rh/$FePO_4$ and 0.8%Rh/$FePO_4$, 0.1 g 0.08%Rh/$FePO_4$, 0.5 mmol quinoline, 5 mL ethanol, 50 °C, 5 bar, dodecane as internal standard.

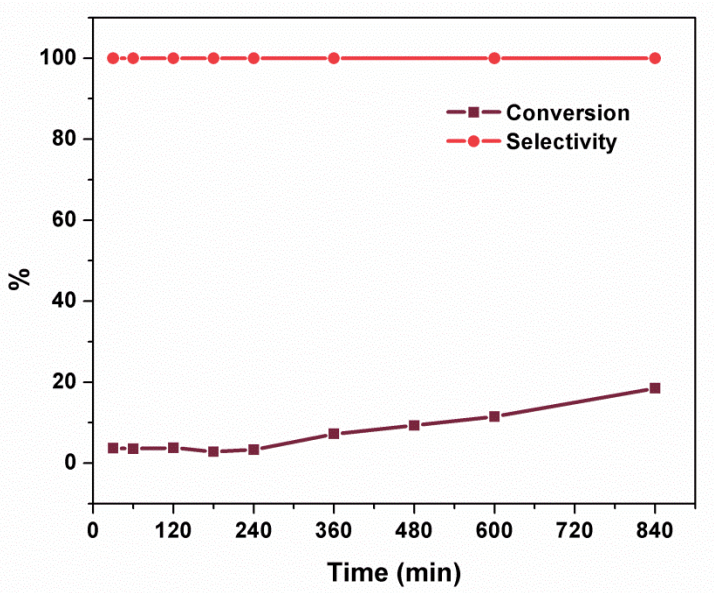

Fig. S5 Kinetic experiment of 0.08%Rh/$FePO_4$ during the hydrogenation of quinoline. Reaction condition: 0.1 g 0.08%Rh/$FePO_4$, 0.5 mmol quinoline, 5 mL ethanol, 50 °C, 5 bar, dodecane as internal standard.

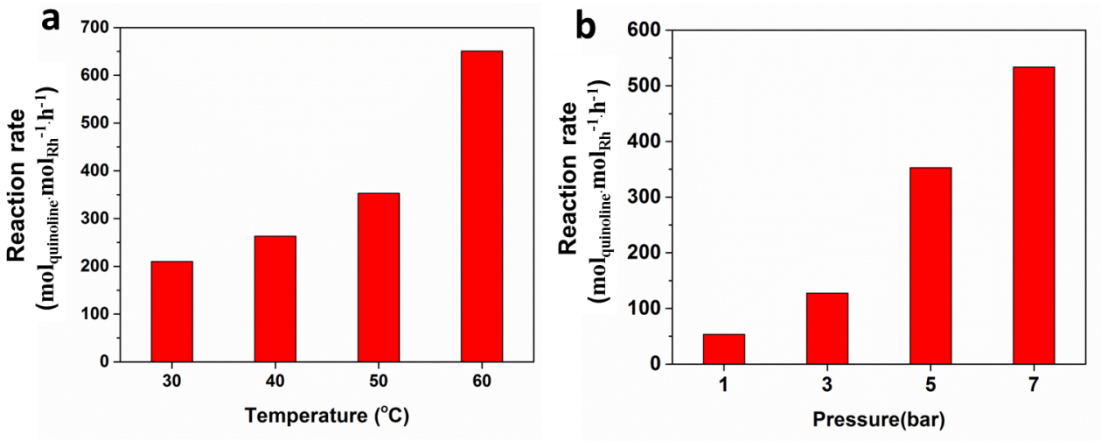

Fig. S6 Effects of temperature (a) and pressure (b) over 0.8%Rh/$FePO_4$ catalyst for the hydrogenation of quinoline.

Reaction condition: 0.05 g 0.8%Rh/$FePO_4$, 0.5 mmol quinoline, 5 mL ethanol, dodecane as internal standard, (a) 5 bar; (b) 50 °C.

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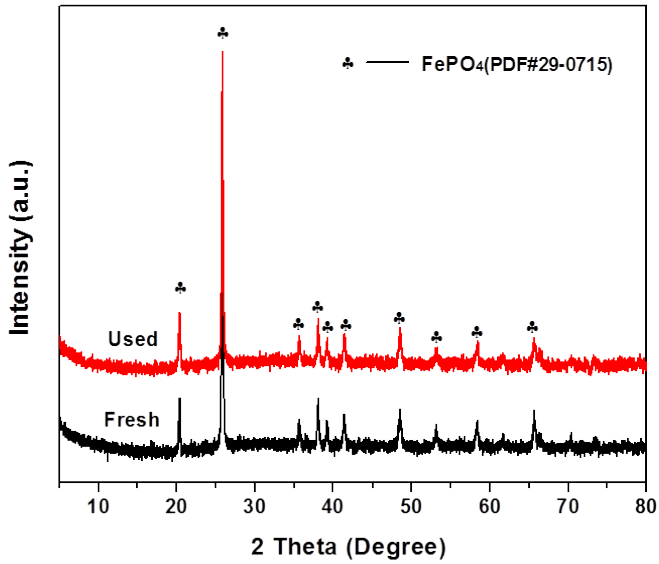


Fig. S7 XRD patterns of the fresh and used 0.8%Rh/$FePO_4$ catalysts. The diffraction peaks belong to the $FePO_4$ support (PDF#29-0715).

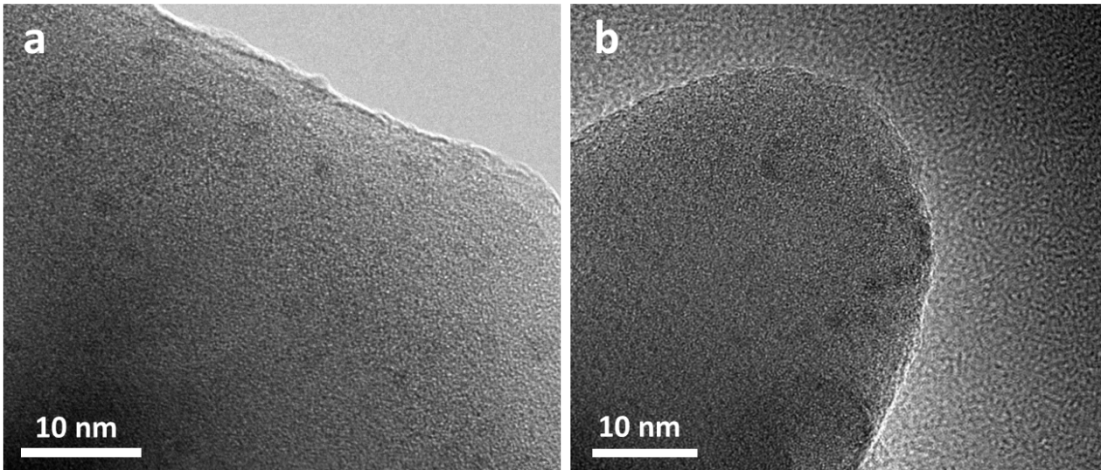


Fig. S8 HRTEM images of the fresh (a) and used (b) 0.8%Rh/$FePO_4$ catalysts. The particle size of metal Rh in the fresh and used catalysts is about 1.0 nm, indicating the high stability of 0.8%Rh/$FePO_4$ for the hydrogenation of quinoline.

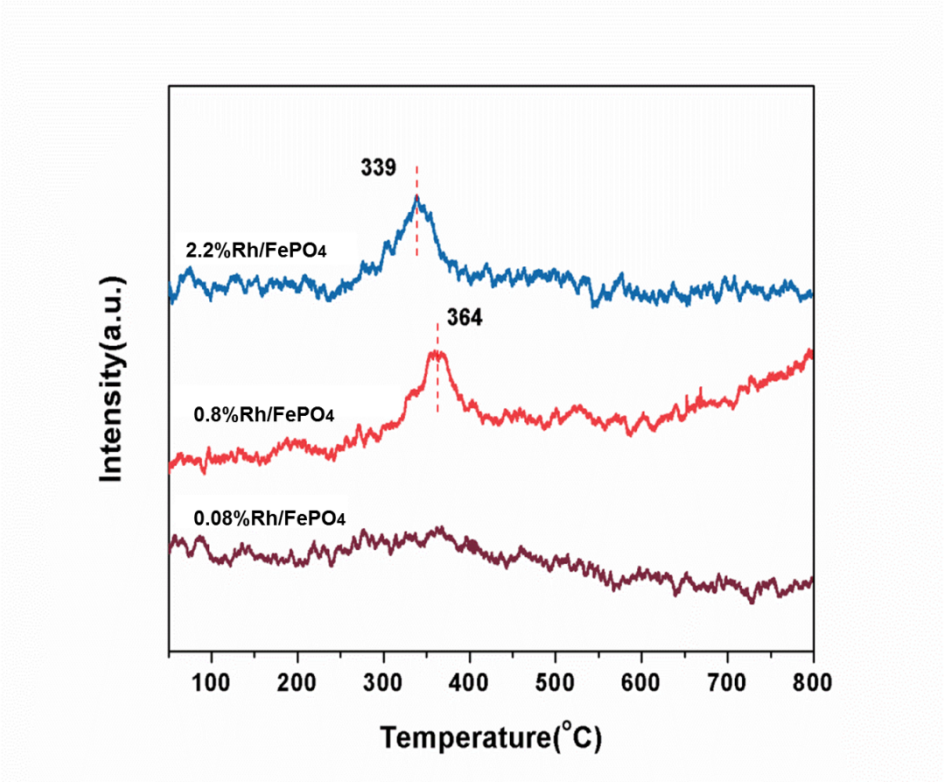


Fig. S9 H_2-TPD results for different Rh/$FePO_4$ catalysts.

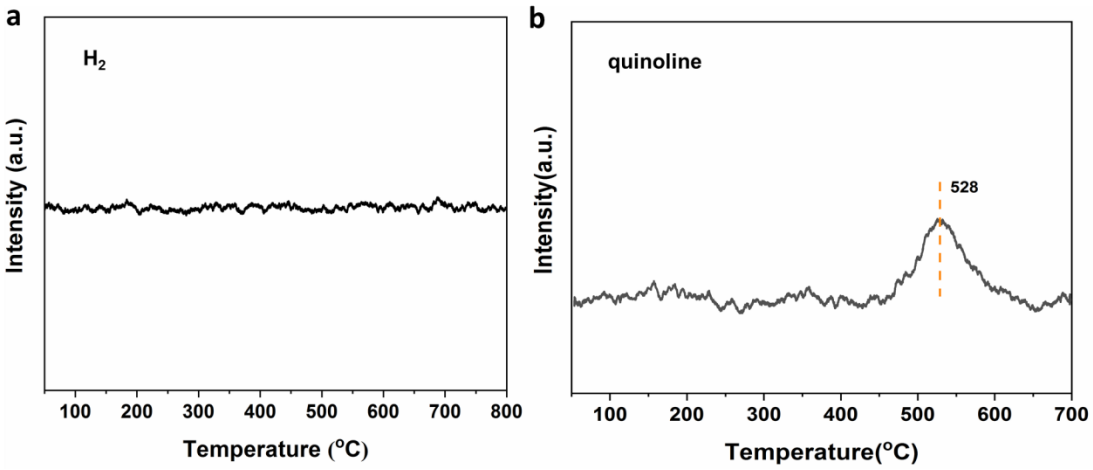


Fig. S10 TPD results of H_2 (a) and quinoline (b) over $FePO_4$ support.

Table S1 IR bands of CO adsorption on the Rh sites over different $Rh/FePO_4$ catalysts.

Catalyst	$Rh(CO)_2$ Symmetric stretching	A_{sym}	$Rh(CO)_2$ asymmetric stretching	A_{asym}	2α(°)
$0.08\%Rh/FePO_4$	2090	0.35	2018	0.33	~88
$0.8\%Rh/FePO_4$	2090	1.5	2018	1.7	~94
$2.2\%Rh/FePO_4$	2092	1.2	2026	2.3	~108

The high and low wavenumber adsorbed peaks in the doublet feature of $Rh(CO)_2$ corresponds to the symmetric and anti-symmetric CO-stretching mode, respectively. The ratio of integrated absorbance (A_{asym}/A_{sym}) is related to the angle (2α) between carbonyl groups[1-2], which follows the formula as $\tan^2\alpha = A_{asym}/A_{sym}$. As shown in Table S1, it is noted that the angle between two CO molecules adsorbed on single Rh atom is estimated to 88 °. The angle becomes larger when the CO molecules are adsorbed on Rh subnano clusters, and further increase to approximately 108 ° on Rh nanoparticles. It is suggested that the geometry of CO adsorption on Rh single atom, subnano cluster and nanoparticle sites is entirely different, in accordance with previous reports[2-3].

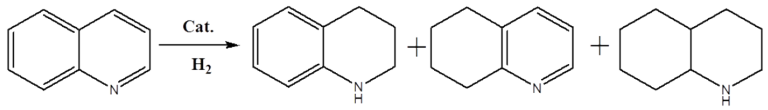
Table S2 The H_2 consumption amount according to the first reduction peak over different $Rh/FePO_4$ catalysts.

Catalyst	Theoretical consumption (mmol/g)	Actual consumption (mmol/g)
$0.08\%Rh/FePO_4$	0.01	1.1
$0.8\%Rh/FePO_4$	0.12	3.3
$2.2\%Rh/FePO_4$	0.32	3.5

Table S3 Representative data for selective hydrogenation of quinoline using noble metal-based heterogeneous catalysts under mild condition.

Catalyst	T (^{o}C)	P_{H2} (bar)	Conv. (%)	Yield (%)	reaction rate $mol_{quinoline} \cdot mol_{Rh}^{-1} \cdot h^{-1}$	Ref.
0.8%Rh/$FePO_4$	50	5	99	>99	353	This work
Pd_0HAP(30)	50	1	98	96	25	[4]
Pd@ompg-C_3N_4	40	1	100	100	7	[5]
PdNPore	25	5	100	93	0.5	[6]
SiO_2@RF/Pt	25	1	>99	>99	15.2	[7]
Pt/TiO_2-ED	30	10	>99	>99	5.8	[8]
Rh/[BMIM][tppm]	50	30	96	96	6.3	[9]

Table S4 Catalytic performance of $FePO_4$ supported different noble metal catalysts.



1 2 3 4

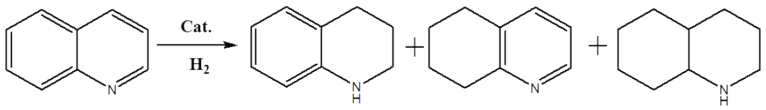
Catalyst	Time (min)	Conv. (%)	Sel.（%）		
			2	3	4
0.5%Pt/$FePO_4$	40	4	>99	0	0
0.5%Ru/$FePO_4$	40	0	0	0	0
0.5%Pd/$FePO_4$	40	0	0	0	0
0.5%Au/$FePO_4$	40	0	0	0	0

Reaction conditions: 0.05 g catalyst, 0.5 mmol quinoline, 5 mL ethanol, dodecane as internal standard, 5 bar, 50^{o}C.

Table S5 Element analysis of different Rh/$FePO_4$ catalysts by XPS.

Element	Atomic %		
	0.08%Rh/$FePO_4$	0.8%Rh/$FePO_4$	2.2%Rh/$FePO_4$
Cl	0.9	3.3	11.1
Fe	5.7	5.7	5.2
O	75.0	71.8	65.1
P	18.2	18.3	15.2
Rh	0.2	0.9	3.4

Table S6 The solvent effect on the hydrogenation of quinoline over 0.8%Rh/$FePO_4$.



1 2 3 4

solvent	Conv. (%)	Sel.（%）		
		2	3	4
Toluene	31	>99	0	0
Cyclohexane	6	>99	0	0
Methanol	88	>99	0	0
Ethanol	99	>99	0	0

Reaction conditions: 0.05 g catalyst, 0.5 mmol quinoline, 5 mL solvent, dodecane as internal standard, 5 bar, 50 ^{o}C.

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